

Determination of the Mg/Mn ratio in foraminiferal coatings: an approach to correct Mg/Ca temperatures for Mn-rich contaminant phases

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Abstract

The occurrence of manganese-rich coatings on foraminifera can have a significant effect on their bulk Mg/Ca ratios thereby biasing seawater temperature reconstructions. The removal of this Mn phase requires a reductive cleaning step, but this has been suggested to preferentially dissolve Mg-rich biogenic carbonate, potentially introducing an analytical bias in paleotemperature estimates. In this study, the geochemical composition of foraminifera tests from Mn-rich sediments from the Antarctic Southern Ocean (ODP Site 1094) was investigated using solution-based and laser ablation ICP-MS in order to determine the amount of Mg incorporated into the coatings. The analysis of planktonic and benthic foraminifera revealed a nearly constant Mg/Mn ratio in the Mn coating of ~0.2 mol/mol. Consequently, the coating Mg/Mn ratio can be used to correct for the Mg incorporated into the Mn phase by using the down core Mn/Ca values of

samples that have not been reductively cleaned. The consistency of the coating Mg/Mn ratio obtained in this study, as well as that found in samples from the Panama Basin, suggests that spatial variation of Mg/Mn in foraminiferal Mn overgrowths may be smaller than expected from Mn nodules and Mn-Ca carbonates. However, a site-specific assessment of the Mg/Mn ratio in foraminiferal coatings is recommended to improve the accuracy of the correction.

1. Introduction

Foraminiferal Mg/Ca ratios show strong temperature sensitivity owing to the temperature-dependent partitioning of Mg during calcification, with more Mg incorporated into the carbonate when ambient seawater temperatures are higher (e.g. Nürnberg et al., 1996; Rosenthal et al., 1997; Lea et al., 1999). During the past two decades, foraminiferal Mg/Ca thermometry has been successfully used to reconstruct past temperature changes in the surface and deep ocean (e.g. Lea et al., 2000; Barker et al., 2009; Elderfield et al., 2012). Reliable seawater temperature reconstructions require the removal of extraneous material that may bias the Mg/Ca ratio away from that of the biogenic carbonate. Cleaning procedures designed for Mg/Ca paleothermometry routinely involve the removal of clays and organic matter (Elderfield and Ganssen, 2000; Barker et al., 2003; Rosenthal et al., 2004). The removal of Mn-rich contaminant phases requires an additional reductive step (Boyle and Keigwin, 1985), but there has been some debate as to whether their removal is necessary. On the one hand, if Mn-rich phases associated with foraminifera have Mg/Mn ratios typical for marine Mn nodules and Mn-Ca carbonates, on the order of 0–0.4 mol/mol (e.g. Cronan, 1975; Peacor et al., 1987; Baturin, 1988; de Lange et al., 1992; Wen et al., 1997), measured Mn/Ca ratios of 0.1 mmol/mol would imply a bias in the original Mg/Ca ratio by only about 0.02 mmol/mol. This is insignificant in most cases and supports the argument for omitting a reductive step (Barker et al., 2003). On the other hand, the potential presence of Mn-rich phases with high Mn/Ca ratios (Boyle, 1983; Pena et al., 2005; 2008) would argue in favor of

the inclusion of a reductive cleaning step (Martin and Lea, 2002; Pena et al., 2005, 2008; Bian and Martin, 2010).

However, the reductive cleaning step has been shown to adversely affect the Mg/Ca ratio of the remaining, cleaned, biogenic carbonate, lowering the Mg/Ca ratio of core-top and low-Mn samples much more than expected from Mg/Mn estimates for the Mn-rich contaminant phase (Barker et al., 2003; Rosenthal et al., 2004; Elderfield et al., 2006; Yu et al., 2007; Yu and Elderfield, 2008; Bian and Martin, 2010). Although there is some debate about the exact mechanism involved (Yu et al., 2007; Bian and Martin, 2010), this offset in Mg/Ca has been attributed to the selective removal of Mg from the carbonate lattice. Incongruent dissolution of carbonates has also been observed during acid leaching experiments and post-depositional dissolution on the sea floor, indicating that Mg-rich carbonate is more dissolution-prone than low-Mg carbonate (Russel et al., 1994; Brown and Elderfield, 1996; Rosenthal et al., 2000; Haley and Klinkhammer, 2002; Benway et al., 2003; Barker et al., 2003; Sadekov et al., 2010; Fehrenbacher and Martin, 2014). Due to the bias introduced by reductive cleaning, it has been recommended to omit this step and to clean foraminifera according to the method published by Barker et al. (2003) (Barker et al., 2003; Yu et al., 2007; Yu and Elderfield, 2008). While this may be a valid approach for most samples considered for paleoceanographic research, there is a need for alternative strategies for samples that are significantly contaminated by Mn-enriched phases.

In this study, we demonstrate that a promising solution to this potential problem is to quantitatively determine the Mg/Mn ratio in the Mn-rich phase of the foraminifera used for Mg/Ca thermometry. The combination of solution-based and laser ablation inductively coupled plasma mass spectrometry (solution-based ICP-MS and LA-ICP-MS, respectively) applied to chemically cleaned Mn-enriched planktonic and benthic foraminifera allows differentiation between the Mg/Mn ratio of the material removed during reductive cleaning and the Mg/Mn ratio of the Mn-rich contaminant. If the coating Mg/Mn is constant over time,

the obtained ratio can be employed to correct for Mg in the contaminant phase using the foraminiferal Mn/Ca down core record following the equation

$$\frac{Mg}{Ca_{corrected}} = \frac{Mg}{Ca_{ox}} - \left(\frac{Mn}{Ca_{ox}} \times \frac{Mg}{Mn_{coating}} \right) \quad (1)$$

where the subscript *ox* represents the *oxidative* cleaning procedure.

2. Study area

The samples selected for this study are from Ocean Drilling Project (ODP) Site 1094 (53.2°S, 05.1°E, water depth of 2807 m) retrieved from the Atlantic sector of the Southern Ocean south of the Antarctic Polar Front. The study site is currently bathed by Circumpolar Deep Water and is well ventilated, sitting immediately downstream of newly formed Antarctic Bottom Water (AABW) (Jaccard et al., 2016). Recent studies have suggested that the deep South Atlantic underwent large changes in oxygenation both on millennial and glacial-interglacial timescales (e.g. Jaccard et al., 2016; Gottschalk et al., 2016). These changes in oxygenation stem from a combination of decreased deep water production and increased organic matter remineralization (and thus oxygen demand) resulting from increased iron fertilization during past ice ages (Jaccard et al., 2016). The sediments are thus characterized by significant changes in redox conditions thereby affecting the sedimentary incorporation of redox-sensitive trace metals, such as Mn and U (Hayes et al., 2014; Jaccard et al., 2016). Jaccard et al. (2016) recently reported substantial sedimentary Mn accumulations during the last glacial termination, illustrating the return to oxic conditions at times when remineralized carbon was released back to the atmosphere. A literature compilation showed that these Mn peaks had previously been reported from South Atlantic sediments and more broadly from the equatorial- and subarctic Pacific (e.g. Jaccard and Galbraith, 2012; Jaccard et al., 2016). As such, the conditions encountered at the study site may be more common than previously assumed.

3. Background and experimental approach

A 1.5 Ma long planktonic *N. pachyderma* (s.) Mg/Ca record (n = 988) has been established at ODP Site 1094 (Figure 1). The foraminifera were picked from a relatively narrow size fraction (mostly 200–250 μm ; on rare occasions 150–250 μm), and cleaned following the protocol outlined by Barker et al. (2003), i.e. omitting the reductive step (see details in Section 4.2). The results reveal a positive correlation between Mg and Mn, over a range of Mn/Ca ratios up to 3.2 mmol/mol (Figure 1a), with shell weight changes having only a small impact on their covariation. Mn/Ca in unaltered planktonic foraminiferal carbonate collected from plankton tows, sediment traps and sediment core-tops (e.g. Boyle, 1983; Russell et al., 1994; Eggins et al., 2003; Barker et al., 2003) are typically well below 0.05 mmol/mol, suggesting that most of the Mn is of post-depositional origin. Application of Mg/Ca paleothermometry (using the calibration by Vázquez Riveiros et al., 2016) to interglacial sequences with high Mn accumulation at this site resulted in unrealistically high sea surface temperatures (SST) of more than 10 °C. This temperature overestimation in sediments with high Mn enrichment, as well as the clear positive correlation of Mg and Mn points to the incorporation of Mg into the Mn-rich contaminant phase.

A closer examination of the correlation between Mg and Mn in Figure 1a shows that only a small portion of the variance can be explained by a linear fit ($r^2 = 0.03$) for samples with Mn/Ca lower than 0.1 mmol/mol. Consequently, Mg/Ca values that are accompanied by low Mn/Ca primarily reflect Mg variations in the calcite lattice that vary with ambient seawater temperature. In contrast, the correlation coefficient for Mn-rich foraminifera samples (Mn/Ca > 0.5 mmol/mol) is relatively high ($r^2 = 0.57$), with Mg/Ca varying primarily due to changes in post-depositional Mn accumulation. Around one third of these Mn-rich samples are from two short-lived spikes within Marine Isotope Stage (MIS) 9 and 11, where Mn/Ca correlates strongly with Mg/Ca ($r^2 = 0.96$ and 0.89 , respectively) (Figure 1b).

The main goal of this study is the analytical determination of the Mg/Mn ratio in the coatings of foraminifera from ODP Site 1094 in order to be able to correct for the Mg present in the Mn-rich phases. The Mg/Mn ratio of the Mn-rich phase can be determined by taking the

difference in Mg/Ca and Mn/Ca between samples cleaned using the oxidative and the reductive cleaning protocol, respectively, and can be obtained by

$$\frac{\Delta x}{\Delta Mn} = \frac{\left(\frac{x}{Ca}\right)_{red} - \left(\frac{x}{Ca}\right)_{ox}}{\left(\frac{Mn}{Ca}\right)_{red} - \left(\frac{Mn}{Ca}\right)_{ox}} \quad (2)$$

where x represents the element of interest, and subscripts *red* and *ox* represent the *reductive* and *oxidative* cleaning procedures, respectively.

The *N. pachyderma* (s.) samples were selected to cover several depth intervals characterized by high Mn levels ($n = 75$, 125–950 ka), representing foraminiferal Mn/Ca ratios ranging from 0.1 to 3.2 mmol/mol (Figure 1a). The experiment conducted on *N. pachyderma* (s.) was complemented by investigation of the planktonic species *Globigerina bulloides* ($n = 10$, 332–401 ka) and *Globorotalia puncticuloides* ($n = 7$, 332–335 ka), and the benthic species *Melonis pompilioides* ($n = 25$, 335–1450 ka) and *Melonis barleeanum* ($n = 2$, 1164–1408 ka) whenever their respective abundances were high enough to allow meaningful analysis. All these samples were analyzed by solution-based ICP-MS to obtain bulk trace element ratios. In addition, five of the samples (0.8–3.2 mmol/mol Mn/Ca), along with two samples with minimal coating (< 0.05 mmol/mol Mn/Ca), were analyzed by laser ablation ICP-MS to investigate the spatial distribution of trace elements within and on the surfaces of the foraminifera.

4. Methods

4.1 Cleaning strategy

The polar species *N. pachyderma* (s.) in sediments of ODP 1094 have very low shell weights (3–10 μg per individual picked from the 200–250 μm size fraction) and are thus prone to dissolution during chemical cleaning. A preliminary test showed that the reductive reagent (Boyle and Keigwin, 1985), applied to a subset of *N. pachyderma* (s.) samples, dissolved more than 80 % of the carbonate for average starting shell weight of less than ~ 7 μg . In this

study, an attempt was made to minimize sample loss by reducing the corrosivity of the reagent applied.

Although reductive cleaning was originally designed to facilitate the removal of Mn and Fe oxides from the test surface by reducing Mn^{4+} and Fe^{3+} to soluble Mn^{2+} and Fe^{2+} (Boyle and Keigwin, 1985), this step has also been shown to be efficient in removing Mn-rich carbonate phases (Pena et al., 2005). The reductive reagent commonly used consists of 31 M hydrous hydrazine (N_2H_4), 16 M ammonium hydroxide (NH_4OH), and a solution of 0.25 M citric acid ($\text{C}_3\text{H}_5\text{O}(\text{COOH})_3$) and 16 M ammonia (NH_3), mixed together in proportions of 1/8:1:1 (Boyle and Keigwin, 1985; Yu et al., 2007). In this study, the concentrations of hydrazine and ammonium citrate (with molarities of 1.75 M and 0.13 M in the standard solution, respectively) were reduced to 50 % and 25 % of their original concentrations in order to decrease citrate-induced carbonate dissolution (Yu et al., 2007; Bian and Martin, 2010). In samples with abundant *N. pachyderma* (s.) and high shell weight (38 of 75 samples), the reductive cleaning step was applied to three subsets of foraminifera samples using three different reductive cleaning solutions: the standard reductive solution, and the two more dilute solutions. Additionally, the “25 %” reductive reagent solution was applied to replicate samples in 28 cases, in order to test the reproducibility of the results. As shown below, the results revealed that the “25 %” reductive cleaning solution was able to remove the majority of the Mn-rich coating, leading to the decision to apply this less corrosive reductive reagent solution to the samples where foraminifera were sparse and/or shell weights were low. Because the planktonic foraminifera *G. bulloides* and *G. puncticuloides* are generally larger and more robust than the *N. pachyderma* (s.) in the samples considered here, they were cleaned using both the standard and “25 %” reductive solution along with some replicates for the latter method where sufficient material was available. The benthic foraminifera were cleaned using the standard reductive cleaning solution only, as a preliminary test revealed that the diluted solutions were not able to remove the Mn phases adequately.

4.2 Cleaning procedures

Depending on their shell weight and the abundance of the foraminifera, a varying number of well-preserved and visibly clean individuals (usually > 300 µg and > 40 planktonic and > 9 benthic individuals) were picked for each of the cleaning procedures applied. The planktonic foraminifera were selected from a relatively narrow size range (*N. pachyderma* (s.): 200–250 µm; *G. bulloides* and *G. puncticuloides*: 355–425 µm), and the benthic foraminifera were picked from the >150 µm size range. Prior to cleaning, foraminifera tests were weighed and gently crushed between two glass plates under a microscope to allow contaminant phases to be removed during cleaning (Boyle and Keigwin, 1985). The crushed material was then transferred to acid cleaned thin walled 500 µl polypropylene vials (Greaves, 2008). The oxidative cleaning procedure applied in this study is that published by Barker et al. (2003). Briefly, clays were removed by multiple rinses with ultra-purified water and methanol. Organic matter was removed by oxidation in a hot alkali-buffered (0.1M NaOH) solution of 1 % hydrogen peroxide (H₂O₂). Subsequently, the test fragments were checked under a microscope to remove any remaining silicates. Finally, samples were leached with 0.001M double distilled HNO₃ to remove any adsorbed contaminants from the foraminifera tests. The reductive cleaning protocol includes all steps described above, but with an additional step to remove trace metal enriched Fe-Mn contaminant phases (Boyle, 1981; Boyle and Keigwin, 1985). Briefly, after the clay removal step, 100 µl of reductive cleaning solution was added to each sample, which was then placed into a hot water bath for 30 minutes.

4.3 ICP-MS analysis

The cleaned foraminifera material was dissolved in ~300 µl 0.1M double distilled HNO₃, centrifuged for 5 minutes (5000 rpm) and transferred to trace-metal cleaned Savillex PFA vials, leaving 30 µl of solution behind to avoid contamination from any non-carbonate solid impurity. Element/Ca ratios were measured by ICP-MS at ETH Zurich using a single collector, high-resolution magnetic-sector Thermo Scientific Element XR instrument. The instrument was tuned for maximum sensitivity, concurrently paying attention to oxide and

hydride production and isobaric and molecular interferences. Samples were introduced into the plasma via a self-aspirating microconcentric nebulizer (flow rate of 100 $\mu\text{l}/\text{min}$) in conjunction with a quartz cyclonic spray chamber. Element/Ca ratios were calculated using a synthetic in-house standard. Results were corrected for instrument and dissolution-acid blank (on average three orders of magnitude smaller than a typical sample). Accuracy and precision of the instrument were assessed by routine measurements of six gravimetrically prepared consistency standards of which two are in-house standards (Mg/Ca and Mn/Ca) and four are standards from the University of Cambridge (Mg/Ca) (Greaves et al., 2005). The standards have a composition similar to foraminiferal carbonate and were run at similar Ca concentrations (Greaves et al., 2005). The consistency standards measured throughout the past 20 months are within $0.9\% \pm 3.6\%$ (2 SD) and $0.6\% \pm 4.2\%$ (2 SD) of the gravimetric value for Mg/Ca and Mn/Ca, respectively. The average long-term reproducibility of Mg/Ca and Mn/Ca is $\pm 2.6\%$ (2 RSD) and $\pm 2.2\%$ (2 RSD), respectively.

4.4 LA-ICP-MS analysis

Laser ablation ICP-MS was performed on oxidatively cleaned foraminifera (excl. leaching; Vetter et al., 2013) from 7 samples selected to cover the entire range of Mn concentration (0.02–3.2 mmol/mol Mn/Ca; Figure 1). The laser ablation system consists of a GeoLas (Coherent) 193 nm ArF excimer laser coupled to an Elan 6100 DRC (Perkin Elmer) quadrupole ICP-MS. The sample was targeted by a laser fluence of $\sim 2\text{ J}/\text{cm}^2$ that ablated a layer 30 μm in diameter and about 0.1 μm in depth from the surface of the foraminifera test with each laser pulse, with a repetition rate of 2 Hz. ^{24}Mg , ^{25}Mg , ^{42}Ca , ^{44}Ca , ^{55}Mn , ^{57}Fe , and ^{238}U were measured by sequential peak-hopping with dwell times of 10–30 ms. The material ablated was carried via He (1.1 L/min gas flow) to the ICP-MS that had been optimized for high sensitivity and a low oxide ratio (ThO/Th of $\sim 0.5\%$). Four whole foraminifera from every sample were targeted at three different chambers, resulting in 12 depth profiles per sample. Additionally, chamber fragments from 3 of the 7 samples were ablated towards both,

the outer and the inner surface. The end of the shell wall was identified as the depth where the ^{44}Ca signal reaches an inflection point (see Figure 4a) (Vetter et al., 2013).

4.5 Scanning electron microscopy

Scanning electron microscopy (SEM) images were obtained using a Zeiss Supra 50 VP, with a secondary electron detector, a working distance of 12 mm, and an accelerating voltage of 15 kV. The cleaned foraminifera fragments were mounted on carbon tape and coated with 10 nm of platinum prior to analysis.

5. Results

5.1 Cleaning efficiency of the reductive cleanings

Mn/Ca and Mg/Ca ratios for *N. pachyderma* (s.), processed without the reductive step, and cleaned using the standard, the “50 %”, and the “25 %” reductive cleaning solution, are shown in Figure 2a–b. Reductive cleaning reduces Mn/Ca concentrations by 87 to 90 %, with gradually increasing efficiency at higher concentrations. For samples with initial Mn/Ca lower than 1 mmol/mol, reductive cleaning reduces Mn/Ca to values generally below 0.1 mmol/mol, independent of the concentration of the reductive solution used (average Mn/Ca after reductive cleaning was 0.05, 0.06 and 0.07 mmol/mol for the standard, “50 %”, and “25 %” reductive cleaning solutions, respectively). In contrast, for samples with initial Mn/Ca ratios ranging between 1 and 3.2 mmol/mol, the standard reductive cleaning solution is slightly more efficient than the more dilute solutions, decreasing Mn/Ca values to an average of 0.13 mmol/mol compared to 0.17 and 0.21 mmol/mol for the “50 %” and “25 %” reductive method, respectively. Insufficient removal of Mn by reductive cleaning may be related to Mn phases that are located in pores and spine holes within the test, whose reductive elimination has been observed to be more difficult (Boyle, 1983; Pena et al., 2005; Pena et al., 2008)

SEM images obtained from oxidatively cleaned *N. pachyderma* (s.) and *G. bulloides* from samples containing high bulk foraminifera Mn concentrations (3.2 and 1.9 mmol/mol Mn/Ca,

respectively) reveal a thin layer at the inner surface of the shell not observed in corresponding tests that have undergone the reductive cleaning step (Figure 2c–d).

5.2 Composition of the material removed during reductive cleaning

The decrease in Mn/Ca in *N. pachyderma* (s.) following the reductive step is accompanied by a significant decrease in Mg/Ca (Figure 2b). Taking the ratio of the differences in Mg/Ca and Mn/Ca between oxidative and reductive cleaning (equation (2)) allows determination of the Mg/Mn ratio of the material removed during reductive cleaning ($\Delta\text{Mg}/\Delta\text{Mn}$). Figure 3a shows the $\Delta\text{Mg}/\Delta\text{Mn}$ ratio for the three reductive cleaning solutions applied as a function of the Mn/Ca difference between the oxidatively and reductively cleaned samples ($\Delta\text{Mn}/\text{Ca}$). The $\Delta\text{Mg}/\Delta\text{Mn}$ ratio decreases with increasing removal of Mn coating, approaching a constant value for $\Delta\text{Mn}/\text{Ca}$ larger than ~ 1.25 mmol/mol. The reproducibility of the $\Delta\text{Mg}/\Delta\text{Mn}$ ratio for the replicated samples, cleaned using the “25 %” reductive method, is relatively high for low $\Delta\text{Mn}/\text{Ca}$, decreasing to 0.04 for $\Delta\text{Mn}/\text{Ca}$ greater than 1.25 mmol/mol. The three different reductive cleaning solutions gave very similar results for samples with high $\Delta\text{Mn}/\text{Ca}$ (Figure 3b). The $\Delta\text{Mg}/\Delta\text{Mn}$ average of *N. pachyderma* (s.) with $\Delta\text{Mn}/\text{Ca} > 1.25$ mmol/mol was 0.25 ± 0.04 ($n = 20$, 1SD), similar to $\Delta\text{Mg}/\Delta\text{Mn}$ for *G. bulloides* (0.23 ± 0.06 , $n = 9$), and *G. puncticuloides* (0.20 ± 0.04 , $n = 3$). The $\Delta\text{Mg}/\Delta\text{Mn}$ values of *M. pompilioides* and *M. barleeaanum* were less dependent on the amount of the Mn phase removed, averaging 0.19 ± 0.04 mol/mol for samples with $\Delta\text{Mn}/\text{Ca} > 0.25$ mmol/mol ($n = 26$). The Fe/Mn ratio of the material removed during cleaning ($\Delta\text{Fe}/\Delta\text{Mn}$) averages 0.02 ± 0.01 ($n = 70$) and 0.04 ± 0.01 ($n = 24$) for planktonic and benthic foraminifera with $\Delta\text{Mn}/\text{Ca} > 0.25$ mmol/mol (Figure 3d).

5.3 Trace element distribution within the foraminifera test

Laser ablation ICP-MS element depth profiles obtained from a series of cleaned *N. pachyderma* (s.) from seven samples provide additional insight into the trace element distribution through the shell wall and its surface. Figure 4 shows a representative selection of depth profiles for three of the five investigated samples, with bulk foraminifera Mn/Ca

281 ranging from 0.8 to 3.2 mmol/mol (Figures 4a–i). The most striking feature in most of the
282 profiles is the systematic increase in Mn/Ca at the inner part of the shell wall, accompanied by
283 a smaller increase in Mg/Ca. In contrast, Fe/Ca is consistently low throughout the entire
284 profile, showing no concurrent trend with Mn/Ca or Mg/Ca (Fe is at or slightly above the
285 detection limit of ~30 ppm; Figure 4c). At the outer part of the shell Mn/Ca is typically an
286 order of magnitude lower than at the inner shell wall, but exceeds the natural range of
287 variability of (uncoated) foraminiferal carbonate from the same site by an order of magnitude
288 (Figure 4j). The accumulation of the Mn phase within the biogenic carbonate makes it
289 practically impossible to define a clear boundary between carbonate and secondary Mn
290 coating, particularly if the Mn enrichment is small (e.g. Figure 4g, 4h). In order to investigate
291 the relationship between Mn and Mg within the higher coated intervals systematically, the
292 Mn-rich part of the depth profile is specified as coating from the point where the Mn/Ca value
293 is twice as large as the test Mn/Ca close to the outer surface (i.e. the average Mn/Ca of the
294 outermost ~1 μm of the profile). Although the definition of the boundary is somewhat
295 arbitrary, it allows us to investigate the Mg/Mn of the Mn phase more quantitatively. From
296 the 86 laser ablation profiles that have been produced on samples with high bulk Mn/Ca
297 values, 49 profiles, measured on 30 different foraminifera, registered an identifiable increase
298 in Mn/Ca.

299 The Mn/Ca profiles within the coated intervals show a gradual increase towards the inner
300 surface where the maximum Mn/Ca ratio is reached (Figures 4a–i). The pattern of Mn/Ca
301 enrichment (gradual to sharp), its lengthscale (~0.2–4 μm), and the values at the inner surface
302 (~1–14 mmol/mol) all show significant variation, even within a single foraminifer. Mg/Mn
303 within the foraminifera tests decreases with increasing Mn concentration, showing ratios of
304 ~0.3–1.4 at the inner surface of the shell (Figures 4a–4i). This large range of Mg/Mn is
305 explained by the variability of Mn/Ca in coatings and its dominant effect on the Mg/Mn ratio.
306 Importantly, coating Mn/Ca and Mg/Mn correlate negatively (Figure 4k–4l). While low
307 Mn/Ca values correspond to Mg/Mn ratios that are very variable, Mg/Mn ratios level off with

higher Mn/Ca. The profiles that resulted from ablation from the inner to the outer surface record higher Mn/Ca values at the inner surface, with their Mg/Mn (~0.2 to 0.4) approaching the value determined by bulk measurements of planktonic and benthic foraminifera.

6. Discussion

6.1 Origin of Mn-rich foraminifera coatings

Mn phases associated with foraminifera tests are Mn-oxyhydroxides and Mn-rich carbonates (Boyle, 1981, 1983; Pena et al., 2005, 2008). As the saturation of seawater with respect to Ca-Mn carbonate requires very high dissolved Mn concentrations (Pedersen and Price, 1982; Landing and Lewis, 1991), sedimentary Mn-rich phases are thought to be originally precipitated as Mn-oxyhydroxides, which then potentially dissolve upon burial and when oxygen-depleted conditions are encountered (Calvert and Pedersen, 1993, 1996). Reduction of Mn^{4+} to soluble Mn^{2+} is a prerequisite for the dissolution of Mn oxyhydroxides, a process that will increase the concentration of dissolved Mn in porewaters (Calvert and Pedersen, 1993; King et al., 2000). Mn is then removed from porewater by the formation of Mn-rich carbonates, preferentially forming at the inner surface of foraminifera tests due to the even more reductive microenvironment (Murray, 1991) and the reactive surfaces that promote nucleation (Pedersen and Price, 1982; Mucci, 2004).

The laser ablation depth profiles through coated tests of *N. pachyderma* (s.) show consistently elevated Mn/Ca values at the inner surface of the shell, corroborating the SEM images that revealed a coating of unknown nature at the inner surface of *N. pachyderma* (s.) and *G. bulloides*. Systematic enrichments in Mn/Ca at the innermost margin of foraminifera shells have also been observed in *Neogloboquadrina dutertrei* from the Panama basin (Pena et al. 2005, 2008). Pena et al. 2005 have identified the Mn phase as a kutnohorite, a Ca-Mn carbonate with typically 5–10 mol% MgCO_3 (Peacor et al., 1987). In contrast to Mn-oxyhydroxides, which are often accompanied by Fe-rich phases, Fe is generally low in Ca-Mn carbonates (Peacor et al., 1987; Calvert and Pedersen, 1996). The present study did not

involve mineralogical analysis of the contaminant phase due to the large amount of foraminiferal material required. However, the suboxic conditions prevailing within the sediments of ODP 1094 (Shipboard Scientific Party, 1999; King et al., 2000) suggest that the Mn-rich contaminant phase is likely a carbonate, as preservation of oxyhydroxides is only possible where the environment remains oxic (Calvert and Pedersen, 1996). This is corroborated by the low Fe/Mn ratios of the material removed during cleaning (Figure 3d) and the lack of correlation between Fe and Mn within the coatings, as shown by the laser ablation profiles (Figure 4c). However, we cannot completely exclude the possibility that a small fraction of the Mn phase is associated with oxyhydroxides.

6.2 Mg/Mn in foraminifera coatings

The Mg/Mn ratio of the material removed during reductive cleaning varies with the amount of Mn-rich contaminant eliminated, leveling off with increasing $\Delta\text{Mn}/\text{Ca}$ (Figure 3a–c). To our knowledge, the only other study that has investigated the effect of reductive cleaning on foraminifera from Mn-rich sediments is that of Pena et al. (2005). Their measurements, conducted on the planktonic foraminifera *N. dutertrei* and *Globigerinoides ruber* from the Panama Basin, show a similar trend, with lower $\Delta\text{Mg}/\Delta\text{Mn}$ values associated with removal of greater amounts of coating material (Figure 3c). Similarly, the $\Delta\text{Mg}/\Delta\text{Mn}$ ratio remains stable for samples with $\Delta\text{Mn}/\text{Ca} > \sim 1.25$ mmol/mol (0.19 ± 0.07), although the range of bulk foraminifera Mn/Ca values is twice as large as in our study. There could be two possible interpretations of the hyperbolic curvature: that the coating Mg/Mn varies with the degree of Mn contamination, or that Mg/Mn is constant in the Mn-bearing phase and another process leads to the observed variation in $\Delta\text{Mg}/\Delta\text{Mn}$.

If $\Delta\text{Mg}/\Delta\text{Mn}$ were controlled only by the variation of Mg/Mn in the Mn contaminant phase, then our results would imply that Mg is less readily incorporated into the Mn phase if Mn concentrations increase in the latter. Mg/Mn ratios in natural Ca-Mn carbonates compiled by Peacor et al. (1987) tend to decrease with higher MnCO_3 contents (Figure 5). Furthermore,

Mucci (1988) showed in laboratory experiments that the amount of Mg incorporated in carbonate overgrowths decreases with increasing MnCO_3 content of the precipitated solid, further corroborating the suggestion that the Mg/Mn ratio in Ca-Mn carbonates decreases with increasing MnCO_3 content (Figure 5b).

While acknowledging that Mg/Mn can vary with the MnCO_3 content, the following arguments argue against substantial variation of MnCO_3 in coatings of foraminifera from ODP Site 1094. First, the strong linear correlation of bulk *N. pachyderma* (s.) Mg/Ca and Mn/Ca in two defined intervals within MIS 9 and 11 indicate that the variation in Mg/Mn in samples from ODP 1094 cannot be large (Figure 1b). Second, a close variation between MnCO_3 content and coating Mg/Mn would imply that $\Delta\text{Mg}/\Delta\text{Mn}$ changes uniformly for all the foraminifera species, and over the entire $\Delta\text{Mn}/\text{Ca}$ range. In contrast, the variation of $\Delta\text{Mg}/\Delta\text{Mn}$ in samples from this study and the Panama Basin where a lot of coating has been removed is small, while the benthic species show almost no variation at all (Figure 3c).

Given that Mg/Mn varies only within a narrow range in the Mn phase accumulating on the inner foraminifera surface, the $\Delta\text{Mg}/\Delta\text{Mn}$ ratio of the samples would be expected to cluster around a nearly constant value. If this assumption is true, then we require another explanation for the variations in $\Delta\text{Mg}/\Delta\text{Mn}$ observed in this study, and in samples from the Panama Basin. Previous studies have demonstrated that Mg is preferentially removed from carbonate during reductive cleaning (e.g. Barker et al., 2003; Rosenthal et al., 2004; Yu et al., 2007; Bian and Martin, 2010), which would result in greater deviation from the Mg/Mn endmember of the Mn coating the smaller the contribution of the contaminant. The coating end member dominates $\Delta\text{Mg}/\Delta\text{Mn}$ with increasing amount of material removed, which constrains the coating Mg/Mn value for all the planktonic foraminifera investigated to 0.24 ± 0.05 , and for the benthic foraminifera to 0.19 ± 0.04 . The good correspondence of the Mg/Mn ratio between the different foraminifera species, which are from sediments whose age ranges from 125 to 1450 ka, indicates that the amount of Mg incorporated into the Mn-rich coatings is species-independent and temporally stable. The slightly lower average of the two benthic

species is consistent with the observation that benthic foraminifera are usually less affected by preferential dissolution during reductive cleaning (Yu et al., 2007; Yu and Elderfield, 2008), implying that their coating Mg/Mn average of 0.19 ± 0.04 is more reliable. This value is close to the average Mg/Mn ratios observed in Mn nodules (Table 1) and Ca-Mn carbonates (Figure 5c).

Laser ablation depth profiles through shells of *N. pachyderma* (s.) reveal great variation in Mn/Ca and Mg/Mn at the inner surface of the shell, within a single profile as well as between profiles from the same foraminifer and sample. However, coating Mn/Ca and Mg/Mn are correlated, with decreasing Mg/Mn ratios for high Mn/Ca values. Given that Mg/Mn in inorganic Mn-rich carbonates coated on foraminifera is consistent across foraminifera species, the variations in Mn/Ca and Mg/Mn might be due to increasing accumulation of the Mn phase in pores close to the inner surface of the test as observed by Pena et al. (2008), leading to an increased proportion of biogenic carbonate ablated with the Mn phase as the inner test surface is approached. Furthermore, the rounded test surface of the small spherical *N. pachyderma* (s.) hinders a perpendicular ablation of the target, increasing the probability of obtaining a mixed signal of primary and secondary carbonate. Last, if ablation starts at the outer surface, the laser beam is forced to pass through the ablation pit before ablating the higher coated intervals, promoting the co-ablation of material from the adjacent shell walls. Notably, highest Mn/Ca ratios at the inner surface are observed if the test is ablated from inner to outer surface. Mg/Mn in these highly coated intervals matches the Mg/Mn range determined by solution-based ICP-MS (Figure 4k–l).

6.3 Preferential dissolution during reductive cleaning

In order to quantify the extent to which Mg is preferentially dissolved from the biogenic carbonate during reductive cleaning, we estimate $\Delta\text{Mg}/\Delta\text{Mn}$ for the *N. pachyderma* (s.) data using the amount of coating removed ($\Delta\text{Mn}/\text{Ca}$), the Mg/Mn determined for the coatings of *N. pachyderma* (s.), and estimates of the decrease in Mg/Ca of the carbonate during reductive

cleaning. The estimated $\Delta\text{Mg}/\Delta\text{Mn}$ is a function of the degree to which Mg is preferentially dissolved and is given by

$$\frac{\Delta\text{Mg}}{\Delta\text{Mn}} = \frac{\text{Mg}_{\text{coating}} + \text{Mg}_{\text{carbonate}}^{\text{lost from}}}{\text{Mn}_{\text{coating}}} = \frac{\Delta \frac{\text{Mn}}{\text{Ca}} a + \left(\frac{\text{Mg}}{\text{Ca}_{\text{ox}}} - \frac{\text{Mn}}{\text{Ca}_{\text{ox}}} a \right) f}{\Delta \frac{\text{Mn}}{\text{Ca}}} \quad (3)$$

where $\Delta\text{Mn}/\text{Ca}$ represents the difference in Mn/Ca between oxidatively and reductively cleaned samples, a denotes Mg/Mn in the coating, the term in brackets represents the estimate for the unaltered Mg/Ca in the carbonate, and f is the proportion of Mg that is preferentially lost from the biogenic carbonate during reductive cleaning (i.e., the extent by which $\text{Mg}/\text{Ca}_{\text{ox}}$ is lowered). The value taken for the coating Mg/Mn (a) is 0.19 mol/mol, the average for Mn-rich coatings associated with the more dissolution-resistant benthic foraminifera from ODP Site 1094. Importantly, the outcome of the calculations is not sensitive to the exact value chosen for a . Mn in biogenic carbonate, typically well below 0.05 mmol/mol Mn/Ca (e.g. Boyle, 1983; Russell et al., 1994; Eggins et al., 2003; Barker et al., 2003), is neglected here due to its minor effect on the results.

Figure 6 shows the estimated $\Delta\text{Mg}/\Delta\text{Mn}$ as a function of 5 %, 15 % and 30 % preferential dissolution of Mg-enriched carbonate along with the analytically determined $\Delta\text{Mg}/\Delta\text{Mn}$ values for each of the reductive cleaning methods (Figure 6a–c) and their averages (Figure 6d). $\Delta\text{Mg}/\Delta\text{Mn}$ estimated assuming that 15 % of Mg is preferentially dissolved agrees well with the analytical data, its linear fit plotting close to the 1:1 line in each of the scatter plots. These results correspond well to previous studies showing that the Mg/Ca ratio of reductively cleaned core top planktonic foraminifera is ~10–15 % lower than those that have only seen an oxidative clean (Barker et al. 2003; Rosenthal et al., 2004, Bian and Martin, 2010). Other studies have shown that reductive cleaning decreases Mg/Ca of benthic foraminifera by ~8 % more than expected from Mg/Mn in Mn phases (Yu et al., 2007; Yu and Elderfield, 2008), in agreement with our assumption that benthic foraminifera are less susceptible to preferential dissolution of MgCO_3 .

Remarkably, the degree to which Mg/Ca is offset from the value expected from the Mg/Mn ratio in the Mn phase does not seem to depend on the corrosivity of the cleaning solution used, although the solubility of carbonates increases with increasing citrate concentration (Yu et al., 2007; Bian and Martin, 2010). This is consistent with cleaning experiments of Bian and Martin (2010) showing that the Mg/Ca offset of foraminifera cleaned with varying citrate concentrations are all very similar, though consistently lower compared to samples cleaned with a solution containing no citrate. The leveling off of Mg/Ca with increasing corrosivity of the cleaning solution suggests that the lowering of Mg/Ca during reductive cleaning does not act like post-depositional dissolution (Brown and Elderfield, 1996; Sadekov et al., 2010). Bian and Martin (2010) invoke other mechanisms to explain the lowering of Mg/Ca in low-Mn samples after reductive cleaning, such as the preferential removal of Mg restricted to the surface or to Mg-enriched portions of the test.

6.4 Implications for paleoceanographic reconstructions of foraminiferal Mg/Ca temperatures

The results presented in this study confirm that Mn-rich contaminant phases associated with foraminifera can have a significant impact on the Mg/Ca ratio of biogenic carbonate. When translated into temperature using the recently published species-specific calibration for *N. pachyderma* (s.) (Vázquez Riveiros et al., 2016), the Mg within the coating can produce a temperature overestimation of up to 7.0 ± 2.2 °C, given the 1σ range of the Mg/Mn ratio in the contaminant phase determined in benthic foraminifera (Figure 7d–f). Using the average Mg/Mn ratio of 0.19 mol/mol, 14 % of the samples analyzed are shown to be contaminated to a degree that leads to a temperature bias of more than 0.9 °C, equivalent to the calibration uncertainty of *N. pachyderma* (s.) (Vázquez Riveiros et al., 2016). To circumvent this problem, we corrected for Mg in the contaminant phase using the downcore Mn/Ca record of the oxidatively cleaned foraminifera samples.

We applied a correction to the 1.5 Ma long *N. pachyderma* (s.) Mg/Ca record from ODP Site 1094, using the average Mg/Mn ratio obtained for benthic foraminifera from the same core. In order to assess the sensitivity of the corrected Mg/Ca to the value for the selected Mg/Mn ratio, Mg/Mn was varied within the 1σ range (Figure 7a–c). The difference between the measured and the corrected Mg/Ca is small for Mn/Ca below 0.2 mmol/mol, equivalent to 0.25 ± 0.14 °C (75 % of all samples). In contrast, the corrected Mg/Ca for samples with Mn/Ca higher than 0.2 mmol/mol show a larger and increasing deviation from the original data, removing the positive trend between Mg and Mn. The degree of offset between measured and corrected data is strongly dependent on the value of Mg/Mn employed, the reasons for which are twofold. Firstly, the high Mn/Ca ratios obtained in this study exert great leverage on the corrected Mg/Ca values. Secondly, the low sensitivity of Mg/Ca to temperature at the lower end of the calibration curve (Vázquez Riveiros et al., 2016) translates small Mg/Ca changes into relatively large temperature changes in these cold Southern Ocean waters.

These observations illustrate the crucial importance of the accurate quantification of the Mg/Mn ratio to correct Mg/Ca. While acknowledging that there might be some variability associated with the incorporation of Mg into the Mn phase, we suggest that the average value of the coating Mg/Mn obtained from the benthic foraminifera, which are less prone to dissolution during reductive cleaning, is the best estimate for the Mg/Mn ratio of the Mn phase in samples from ODP Site 1094. Correcting Mg/Ca using Mg/Mn = 0.19 mol/mol eliminates the positive correlation between Mg and Mn observed in the oxidatively cleaned samples with Mn/Ca > 0.5 mmol/mol (slope: 0.02; $r^2 = 0.02$) (Figure 7b).

7. Conclusions

SEM images and laser ablation ICP-MS profiles through foraminifera shells reveal Mn-rich coatings at the inner surface of planktonic foraminifera from the Antarctic Southern Ocean that can have a significant effect on the bulk foraminiferal Mg/Ca ratio. The removal of this

Mn phase requires a reductive cleaning step, but this is known to preferentially dissolve Mg-rich biogenic carbonate. In this study, two different approaches were adopted to assess the coating Mg/Mn in foraminifera from ODP Site 1094 in the Southern Ocean. First, solution-based ICP-MS measurements of oxidatively and reductively cleaned Mn-rich foraminifera allowed determination of the Mg/Mn ratio of the material removed during reductive cleaning. Second, laser ablation ICP-MS provided high-resolution trace element profiles through coated foraminifera shells, corroborating the Mg/Mn results obtained from bulk measurements. The determination of the Mg/Mn ratio in foraminiferal coatings allows correction for Mg incorporated into the Mn phase, by using the down core Mn/Ca record of oxidatively cleaned samples from the same site.

Considering the various sources of Mn in the ocean and sediment, and the occurrence of foraminiferal Mn overgrowths as both oxide and carbonate phases whose formation involves very different processes, the incorporation of Mg into Mn-rich foraminiferal coatings is not expected to be spatially constant. However, coating Mg/Mn ratios observed in samples from the Panama Basin and the Antarctic Southern Ocean are very similar, which render it probable that the range of Mg/Mn in foraminiferal Mn overgrowths is smaller than expected from Mn-rich nodules and Mn-Ca carbonates (~0–0.4 mol/mol). In order to be able to make a broader assessment of the variations in the Mg/Mn ratio in foraminiferal coatings, more studies from other oceanic regions with high Mn accumulation rates would be required.

We recommend application of the protocol presented in this study when foraminiferal Mn/Ca is high enough to introduce a significant bias to measured Mg/Ca ratios and the temperatures calculated from them, for example, in excess of the calibration uncertainty of the species investigated (e.g. 0.9 °C for *N. pachyderma* (s.); Vazquez et al., 2016). There is, however, no absolute Mn/Ca ratio that can be taken as a threshold to indicate a ‘contaminated’ sample because the degree of contamination depends on several factors such as the average Mg/Ca ratios and the temperature sensitivity of the foraminifera species investigated.

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Captions

Table 1. Average Mg/Mn ratios in Mn nodules and Mn encrustations of the Atlantic, Indian, and Pacific Oceans, and the average for the global ocean. Mg/Mn ratios of individual sites can deviate markedly from the basin average.

Figure 1. (a) Covariance between Mg/Ca and Mn/Ca measured in oxidatively cleaned *N. pachyderma* (s.) from sediments of ODP Site 1094, covering the past 1.5 Ma. The linear fits show the correlation between the two parameters at the lower (< 0.1 mmol/mol; $r^2 = 0.03$) and upper end (> 0.5 mmol/mol; $r^2 = 0.57$) of the Mn/Ca range. The white, blue, yellow, and gray symbols show *N. pachyderma* (s.), *G. bulloides*, *G. puncticuloides* and *M. pompilioides* samples that were used in this study. The red stars mark samples that have been investigated by LA-ICP-MS. (b) Correlation of Mg/Ca and Mn/Ca for two short-lived Mn spikes within MIS 9 (open symbols) and MIS 11 (solid symbols).

Figure 2. (a–b) Mn/Ca and Mg/Ca ratios for *N. pachyderma* (s.) after cleaning with three different reductive solutions, compared to samples that have only been cleaned oxidatively. Reductive cleaning results in a clear decrease in Mn/Ca (87–90 %) and Mg/Ca ratios (each of the gray lines represents the results of a sample). (c–d) SEM images of an oxidatively cleaned *N. pachyderma* (s.) and *G. bulloides* chamber fragment with high bulk Mn/Ca values show a distinctive layer at the inner surface of the test. In contrast, SEM images of the same samples after the reductive cleaning step show no evidence of such a layer, indicating that the Mn coating at the inner surface of the test has been successfully removed.

Figure 3. The Mg/Mn and Fe/Mn ratio of the material removed during reductive cleaning ($\Delta\text{Mg}/\Delta\text{Mn}$, $\Delta\text{Fe}/\Delta\text{Mn}$) as a function of the amount of Mn/Ca removed. (a) $\Delta\text{Mg}/\Delta\text{Mn}$ of the different reductive cleaning solutions applied to samples of *N. pachyderma* (s.). (b) Average $\Delta\text{Mg}/\Delta\text{Mn}$ of the reductive cleaning solutions for *N. pachyderma* (s.) compared to $\Delta\text{Mg}/\Delta\text{Mn}$ of the planktonic species *G. bulloides*, and *G. puncticuloides*, and the benthic species *M. pompilioides* and *M. barleeianum*. (c) Compilation of $\Delta\text{Mg}/\Delta\text{Mn}$ data presented in this study

and samples from the Panama Basin (ODP 1240), on the latter for planktonic *N. dutertrei* and *G. ruber* (Pena et al., 2005). (d) $\Delta\text{Fe}/\Delta\text{Mn}$ of planktonic and benthic foraminifera from this study.

Figure 4. Representative selection of laser ablation ICP-MS Mg/Ca (black), Mn/Ca (red), and Mg/Mn (blue) profiles from reductively cleaned *N. pachyderma* (s.) samples of four intervals covering the entire range of Mn/Ca (0.02–3.2 mmol/mol) (a–j). In the first three rows, the two plots on the left show profiles that were produced within a single foraminifer by ablating towards the inner surface (a, b, d, e, g, h, j). Samples plotted in the third column were ablated towards the outer surface (c, f, i). The ^{44}Ca profile, with an example shown in (a), was used to identify the beginning and the end of the shell wall. The dashed line marks the boundary between primary shell and coating, defined as the depth when Mn/Ca reaches twice the value at the outer part of the shell. The example Fe/Ca data shown in (c) are at or only slightly above the detection limit (~30 ppm). Note the different scales on the y-axes. (k) Negative correlation between coating Mg/Ca concentrations and coating Mg/Mn ratios for all measurement points within the coated intervals. (l) Negative correlation between average coating Mg/Ca concentrations and average coating Mg/Mn ratios. The blue and yellow bars in Figure (k) and (l) represent the coating Mg/Mn 1σ range determined by solution-based ICP-MS for planktonic and benthic foraminifera.

Figure 5. (a) Compilation of natural Ca-Mn-Mg carbonates whose composition has been projected onto a CaCO_3 - MnCO_3 - MgCO_3 ternary phase diagram (replotted from Peacor et al., 1987). (b) Mg/Mn of all carbonates from the ternary phase diagram as a function of their MnCO_3 content. Carbonates with 0.5–20 mole% Mg and 1–95 mole% Mn are highlighted in black. Compositions of carbonates that have been precipitated during lab experiments from artificial seawater using different Mn concentrations are shown in red (Mucci, 1988). The legend in (b) is also valid for (a). (c) Histogram of Mg/Mn values in natural Ca-Mn-Mg carbonates with 0.5–20 mole% Mg and 1–95 mole% Mn. Three of the 239 samples, with $\text{Mg/Mn} > 1$, were excluded in calculating the Gaussian fit and the average Mg/Mn ratio.

Figure 6. Assessment of preferential dissolution for *N. pachyderma* (s.) during reductive cleaning for the three different cleaning solutions applied (a–c), and the average of the cleaning solutions (d). The Mg/Mn ratio of the material removed ($\Delta\text{Mg}/\Delta\text{Mn}$) is estimated by using the determined Mg/Mn ratio of the coating and by varying the relative amount of Mg that is preferentially dissolved between 5 % and 30 %. Comparison between the analytically determined and estimated $\Delta\text{Mg}/\Delta\text{Mn}$ indicates that 15 % of the Mg in the carbonate is dissolved during reductive cleaning, its linear fit plotting close to the 1:1 line in each of the scatter plots (see insets). The percentage of Mg dissolved from the carbonate is independent of the corrosivity of the solution used.

Figure 7. (a–c) Covariance between the measured Mg/Ca and Mn/Ca on the one hand (black), and the corrected Mg/Ca and measured Mn/Ca on the other hand (yellow). The linear fits indicate the correlation of Mg/Ca and Mn/Ca for Mn/Ca > 0.5 mmol/mol before (black) and after correction (red). (d–f) Mg/Ca temperature overestimation owing to Mg incorporated into the Mn phase as a function of the measured Mn/Ca. Correction is based on (a, d) the lower bound, (c, e) the average, and (c, f) the upper bound of the obtained 1σ range of Mg/Mn.